(51) International Patent Classification 6 :		(11) International Publication Number:	**WO 98/03695**
C23C 14/22	A1	(43) International Publication Date:	29 January 1998 (29.01.98)

(21) International Application Number: PCT/CA97/00527

(22) International Filing Date: 23 July 1997 (23.07.97)

(30) Priority Data:
08/681,434   23 July 1996 (23.07.96)   US
2,182,452   31 July 1996 (31.07.96)   CA

(60) Parent Application or Grant
  (63) Related by Continuation
    US   08/681,434 (CIP)
    Filed on   23 July 1996 (23.07.96)

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,
GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ,
PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,
TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH,
KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ,
BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE,
CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL,
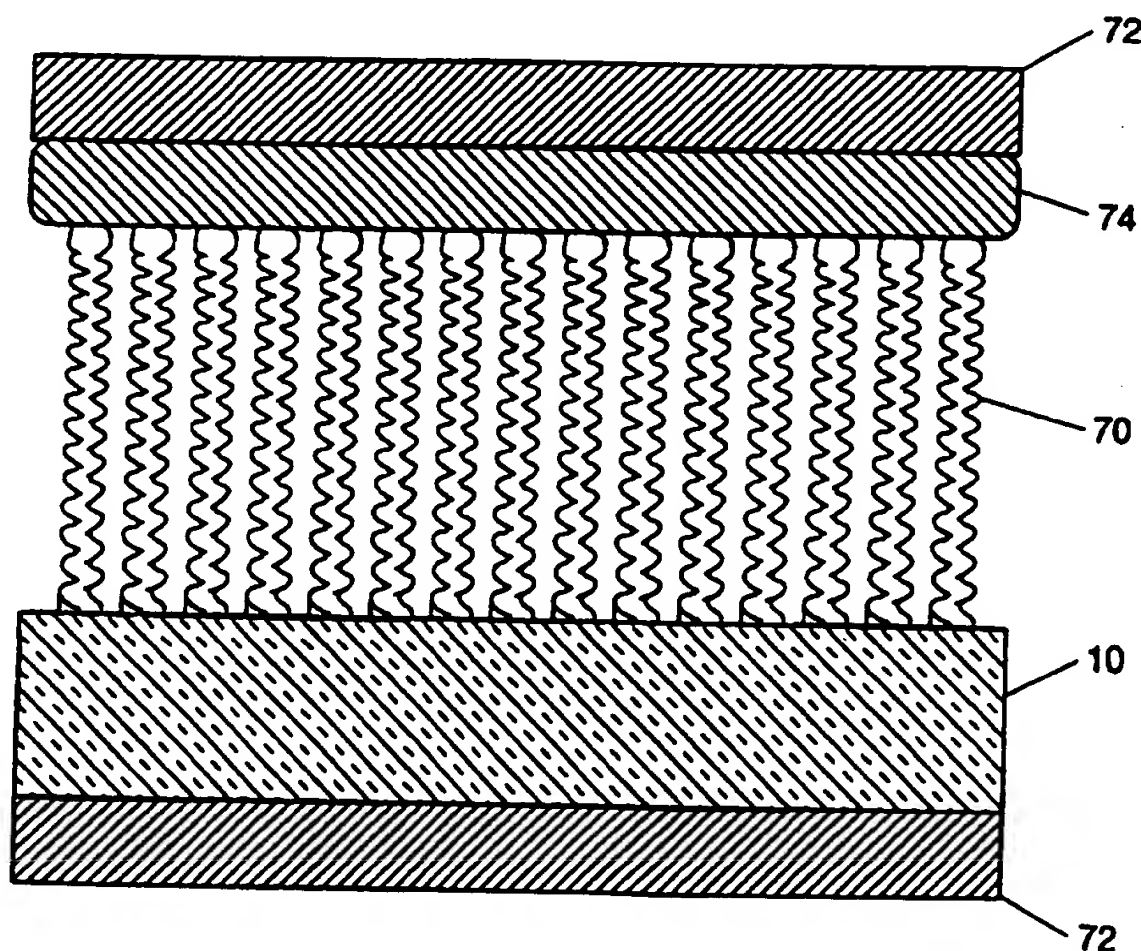PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN,
ML, MR, NE, SN, TD, TG).

(54) Title: CAPPED POROUS THIN FILMS

(57) Abstract

A method of making vapor deposited thin films by rotating a substrate in the presence of an obliquely incident vapor flux. The substrate may be rotated about an axis normal to the surface of the substrate and/or parallel to the surface of the substrate by two motors mounted with their axes orthogonal to each other. A cap is formed on the thin film, for example by increasing the diffusion length of the material being deposited or by rotating the substrate about a plane parallel to the substrate (equivalent to changing the angle of incidence of the vapor flux). Feedback from a deposition rate monitor allows control of rotation speed of both motors to produce a growth with a defined pattern.

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TITLE OF THE INVENTI N:

Capped Porous Thin Films

FIELD OF THE INVENTION

This invention relates to the deposition and
capping of thin films on substrates.

CLAIM TO COPYRIGHT

BACKGROUND OF THE INVENTION

In the art of growing thin films, it is known to
expose a substrate to an oblique incident vapor flux in
conditions of limited adatom diffusion and thus grow a
columnar microstructure on the substrate.

The optical properties of the resulting
microstructure are dependent in part on the material used,
the porosity of the microstructure and the orientation of
the columns of the thin film.

Hamaguchi et al, United States patent no.
4,874,664, describe lateral shifting or rotation of the
position of the substrate in relation to the vapor flux to
create uniform film growth and film layers that have
columns with different orientations in the different
layers. In Hamaguchi et al, the entire substrate is rotated
in between periods of exposure of the substrate to vapor
flux, or the substrate is laterally shifted during exposure
to vapor flux.

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The angl of the incident vapor flux in the prior art tends to be in the range from near 0° to 70° where the angle is measured between the vapor arrival line and the substrate normal, which may be referred to as the polar angle. For stationary substrates, results have been published for polar angles reaching close to 90°. The angle of growth of the columns is related in a way poorly understood to the angle of incidence of the vapor flux, but is always observed to be smaller, as measured from the substrate normal, than the angle of incidence.

A paper of Azzam, "Chiral thin solid films", Appl. Phys. Lett. 61 (26) 28 December 1992, has proposed rotation of the substrate while it is exposed to the oblique incident vapor flux to generate a helical microstructure having helicoidal bianisotropic properties. The proposed rotation of the substrate is about an axis perpendicular to the surface of the substrate, which is referred to in this patent document as rotation about the azimuth, or variation of the azimuthal angle. No particular polar angle is specified, though a figure shows an angle of less than 60°.

The inventors have also proposed improvements to the methods of Azzam and Hamaguchi, as described in "First thin film realization of a helicoidal bianisotropic medium", Kevin Robbie and Michael J. Brett, Akhlesh Lakhtakia, J. Vac. Sci. Technol. A 18(6), Nov/Dec 1995, p. 2991 - 2993. In this article, the inventors demonstrate growth of a helicoidal thin film.

SUMMARY OF THE INVENTION

This invention seeks to overcome some of the limitations of the prior art and provide a film forming system method and apparatus that allows for the growth of

capped complex microstructures. A method is provided for capping a porous columnar microstructure with a dense film.

Therefore, in accordance with one aspect of the invention, there is provided a method of sculpting vapor deposited thin films, the method comprising the steps of initially exposing a surface of a substrate to a vapor flux at an oblique incident angle to grow a columnar thin film and then capping the thin film.

A cap may be formed by rotating the substrate about an axis parallel to the plane of the substrate while exposing the substrate to vapor flux. During capping in this manner, the substrate may be rotated about an axis perpendicular to the plane of the substrate.

A cap may also be formed by exposing the substrate to a vapor flux in conditions of high diffusion length, such that a dense uniform mass is obtained, such as by heating the substrate to nearly the melting point of the material forming the vapor flux.

In a further aspect of the invention, there includes the step of, while initially exposing the substrate to vapor flux, moving the substrate to alter the direction of growth of the columns, as for example by rotating the substrate about a normal to the surface of the substrate to create a helical film growth.

In a further aspect of the invention, a thin film microstructure is provided wherein vapor deposited material extends in distinct columns from a substrate. The columns are capped, and may be supplied with electrodes to form for example a delay line or a variable wavelength optical filter.

In a still further aspect of the invention, the substrate may be provided with small mounds spaced sufficiently close together that growths are confined to grow on the mounds and not between them. In this way, the

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spacing of the helical growths can be determin d in advance of deposition.

These and other aspects of the invention are described in the detailed description of the invention and claimed in the claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

There will now be described preferred embodiments of the invention, with reference to the drawings, by way of illustration, in which like numerals denote like elements and in which:

Fig. 1 is a schematic illustrating prior art understanding of how shadow sculpting forms columnar film microstructures;

Fig. 2 is a schematic showing apparatus according to one aspect of the invention for depositing a thin film on a substrate using a vapor flux, with an exemplary substrate shown in side view, thereby illustrating how polar angle variation alters the incidence of the vapor flux;

Fig. 3 shows the apparatus of Fig. 2 with the substrate in plan view, thereby illustrating rotation of the substrate about a normal to the plane of the substrate;

Fig. 4 shows control elements for use with the apparatus of Figs. 2 and 3;

Fig. 4A shows an arrangement of the azimuthal and polar angle control motors;

Figs. 5A, 5B, 5C and 5D are graphs illustrating polar (Figs. 5A, 5B and 5C) and azimuthal (Fig. 5D) angle variations;

Fig. 6 is a scanning electron micrograph showing helical columns of MgF_2;

Fig. 7A is a side view of a thin film with helical growths deposited on a substrate;

Fig. 7B is a side view of a thin film as in Fig. 7A with a cap, showing electrodes schematically (the electrodes are not necessarily to scale, since in practice each electrode could cover thousands of helixes);

5   Fig. 7C is a side view of the thin film of Fig. 7B with electrode plates bounding the structure;

Fig. 7D is a side view of a film with cap and electrodes;

Fig. 8 is a side view of a substrate with mounds 10   for pre-determining the location of helical growths; and

Fig. 9 is a plan view of a substrate with mounds showing one particular pattern of mounds.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15   Fig. 1 illustrates the physical process underlying growth of a slanted columnar film microstructure as is known in the prior art. A substrate 10, for example a silicon wafer, has a surface 12 with normal N and is exposed to an oblique incident vapor flux 14 whose angle of 20   incidence, defined in relation to the normal N, is θ. As atoms in the vapor flux 14 are deposited onto the substrate 10, film growth areas atoms shadow adjacent regions 16, preventing deposition of vapor in these regions. Atoms in the vapor flux 14 continue to be deposited in regions that 25   are not shadowed, thus forming columns 18. Atoms diffuse adatomically across the tops of the columns as shown at 19. Slanted columnar microstructures will grow if the angle θ is sufficiently large to create the shadowing effect, and there is limited adatom diffusion 19, such that adatom 30   diffusion does not fill in the gaps between columns. In practice, angle θ need only be slightly above 0° to form reasonably defined columns and columnar structures will form in many substances at θ = 0°, though they may be hard to discern under conditions such that the films have high

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atom diffusion lengths, for example due to high temperatures or materials with low melting points. The angle β of the axis of the columns 18 to the normal N of the substrate is less than θ. The actual relationship
5   between θ and β is poorly understood, but approximations of the relationship are known in the art.

"Oblique" as used in this patent document in relation to an angle means sufficiently departing from $0°$ that atomic shadowing has an effect on the growth of
10   columnar microstructures. The substrate may be any solid material on which a vapor may be deposited, and will depend on the application. Silicon substrates will be commonly used. The material to be deposited may be any material for which conditions are achievable to support vapor generation
15   and deposition of the vaporized material on the substrate. In some cases, this may require cooling or heating of the substrate. To assist in bonding one vaporized material to another, an intervening layer may be first deposited, as for example using a chromium intermediate layer to bond
20   gold to amorphous silicon dioxide (glass). The processes described here should be carried out in conditions in which the vapor flux arrives at the substrate in approximately a straight line. For this reason, it is preferred that the process be carried out under conditions approximating a
25   vacuum, at less than 10^{-3} torr, for example at 10^{-6} torr. At higher pressures, scattering from gas molecules tends to prevent well defined structures from growing. In addition, the material used should have a sticking co-efficient of at least about 0.9 to enable the formation of distinct
30   structures.

Referring now to Figs. 2, 3 and 4, an apparatus for capping a film according to the invention is shown for growing a thin film on a substrate 10 having a surface 12. A conventional vapor source 22 is located within a vacuum

chamber 20. A conv ntional shutter (not shown) located above the vapor source 22 is used to control whether or not the substrate 10 is exposed to vapor. Various conventional means (not shown separately) for causing the vapor source 22 to emit a vapor flux 14 may be used. A substrate 10 is supported in the vacuum chamber 20 on a motor 24 (Fig. 4) disposed in the vacuum chamber 20 above the vapor source 22. The motor 24 rotates the substrate about an axis A lying parallel to and preferably in the plane defined by the surface 12 of the substrate 10. Rotation of the substrate 10 about axis A alters the polar angle, namely the angle of incidence θ of the vapor flux 14. Motor 26, also disposed in the vacuum chamber 20 above the vapor source 22, has a rotational axis coinciding with the normal N of the substrate 10 and thus alters the azimuthal angle. The polar angle and the azimuthal angles are both measures of the orientation of the surface of the substrate to the incident flux.

As shown in Fig. 4A, the substrate 10 is preferably mounted on a disc 11 which is attached to motor 26. Various mounting arrangements of motor 24 and motor 26 may be used. For example, motor 26 may be mounted on a frame 25, and the frame 25 may be mounted to rotate with the drive shaft 27 of motor 24. Motor 24 itself may be mounted by any of various conventional methods for mounting motors within a vacuum chamber such as on a support 29.

Referring now to Fig. 4, motors 24 and 26 are preferably conventional stepper motors driven by stepper motor drive electronics 28 and controlled by computer controller 30. The computer controller 30 includes a data acquisition board 32 and a software based interface 34 such as LabVIEW™ available from National Instruments. The data acquisition board 32 receives signals indicative of thin film growth on the substrate output from a deposition rate

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monitor 36 of conventional construction located within the vacuum chamber 20 in a location in which film growth on the deposition rate monitor 36 is representative of film growth on the substrate 10. In response to receiving the output signals from the deposition rate monitor 36, the computer controller 30 instructs the driver 28 to cause the motors 24 and 26 to rotate according to a desired pattern. As described herein, the computer automatically controls the rate of change of the orientation of the surface in response to the output control signals to grow the thin film according to the desired pattern. An exemplary software program for programming the computer controller 30 using LabVIEW™ software is contained in Appendix A. Start and stop signals for vapor deposition may be sent by the computer to a drive for the shutter for starting vapor deposition, or the shutter may be opened manually. Normally, the motors are started before the shutter opens to initiate deposition.

The software receives a deposition rate from the deposition rate monitor. The actual thickness (T2) of the film growing on the substrate is related to the thickness on the deposition rate monitor by an empirically determined scaling factor known as the tooling factor. The software also knows the motor positions at the last time instant (Xfi for motor 24, Xci for motor 26) and receives as input from the operator, the number (N) of turns to be made by the motor 26, the tooling factor (ratio of vertical film growth rate to measured deposition rate), an initial deposition rate estimate, an initial angle of incidence for the vapor flux during sculpted film growth, motor rotation direction, and various parameters that define the desired pattern of growth for the film. The inputs to the computer establish the desired pattern of film growth.

In the case of formation of helical film growths, the pitch w of the helix must be specified, and in the case of a capping layer for a film growth, both the cap thickness (Tc) and number of turns (Nc) of the motor 24 must be specified by the operator. A cap for a columnar thin film is a continuous layer that forms a bridge between the ends of columns remote from the substrate. Due to its continuous nature, the cap is typically considerably more dense than the columnar thin film but may have a limited degree of porosity.

In an embodiment of the invention, the motors 24, 26 are step motors that rotate a fraction of a circle each time instant, ti, ti+1, ti+2 etc. At any given time ti, the computer has just updated the thickness of the film from the deposition rate monitor 36 and changed the motor step rate so that at ti+1, the motor 24, 26 will be at approximately the desired position according to the desired pattern. Between time instants ti and ti+1, the software calculates what the thickness of the film growth will be at ti+2 and calculates how fast the motors must rotate in order to give the desired thickness at ti+2. At ti+2, the computer then reads the new thickness from the deposition rate monitor as well as the motor stepping rates, and adjusts the motor stepping rate so that at ti+3 the film growth pattern will be approximately as desired. The software continues in this fashion until a stop signal is received, for example when the film has reached a desired thickness.

Algorithms for controlling the motors 24, 26 in the case of a helical film with a cap are incorporated in Appendix A, and illustrated graphically in Figs. 5A-5D. For the motor 26, if helical film growth has not reached the desired thickness, that is, T2 is less than w*N, where * indicates multiplication throughout this patent document,

then Xc2 is 360°/w*T2, that is, the substrate 10 is rotated
to a position equal to 360° times the ratio of T2 to w. If
T2 is greater than or equal to w*N, that is, the helical
film thickness has been achieved, then during a capping
5   process, Xc2 is 360*N+360*Nc/Tc*(T2-w*N), that is, Xc2
gradually increases from 360*N to 360*(N+Nc) proportionally
to the capping layer thickness (T2-w*N). This rotation rate
will typically be faster than the rotation rate during
helical film growth, depending on the choice of the factor
10   Nc/Tc.

       For the motor 24, if helical film growth has not
reached the desired thickness, the motor 24 does not change
position, hence polar or flux angle remains the same. If T2
is greater than or equal to w*N, then the new motor
15   position Xf2 equals the motor position at the last time
instant (Xfi) plus (90 - Xfi) times the ratio of the
difference of T2 from w*N to the thickness of the cap (that
is, Xfi = Xfi + (90 - Xfi)/Tc*(T2-w*N).

       This last formula is represented graphically in
20   Fig. 5A. The polar angle (angle of incidence measured from
the normal) is kept constant over an initial period 40,
during which the surface of the substrate is exposed to
oblique incident vapor flux, and then rotated at a constant
angular rate to zero, while continuing to expose the
25   surface to vapor flux. Changing of the polar angle towards
zero produces a cap for the sculpted film growths. At zero
polar angle, the flux is normally incident. The algorithm
for controlling the azimuthal angle results in the
substrate rotating N times to achieve a helical film growth
30   of thickness T2 = w*N. During the capping process, the
substrate continues to rotate about the azimuth, typically,
but not necessarily, at a faster rate than during helical
film growth. During the period 40, the substrate 10 may be
(a) rotated about a normal to its surface to create helical

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microstructures, (b) shifted 180° to form zig-zags, (c) translated, (d) kept at a constant orientation to the vapor source, or (e) otherwise rotated or translated to obtain a desired growth pattern under the cap.

5   Alternatively, the cap for a film growth may be created by exponentially decreasing polar angle as illustrated in Fig. 5B. The algorithm for controlling the polar angle is the same during helical film growth as for the linear cap: the angle is the kept constant. During
10 capping, Xf2 is assigned the value Xfi plus (90-Xfi) times e raised to the power of ((T2-w*N-Tc)/k), where k is the exponential scale factor or time constant (for example, 800). Hence, the polar angle drops monotonically from near 90° to zero as T2 approaches the sum of w*N (the desired
15 thickness of the columnar layer) and Tc (the thickness of the cap). As illustrated in Fig. 5B, polar angle is constant during helical film growth (area 44) and exponentially decreasing to zero in area 46. Rotation speed of the substrate about its normal depends in part on the
20 deposition rate. For MgF_2 at 85° angle of incidence, and a pitch of about 50 nm, the speed is about 2 rpm. Typical rotation speeds used in the process are about 0.2 to 3 rpm. For higher deposition rates, higher speeds will be possible, but the speed should not be so high so as to
25 destroy the distinct columnar features produced by the invention. Although decreasing the polar angle linearly with time also increases the density of the cap layer, it is preferred to use an exponential decrease, wherein the rate of decrease increases with time, since that appears to
30 reduce the probability of high stress in the cap that may lead to fracture.

        Fig. 7A illustrates a thin film microstructure produced by the process described here with rotation of the substrate about a normal to the substrate. Vapor deposited

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material xtends in distinct (separate from one another) helical columns 70 from the substrate 10. Fig. 7B illustrates the same thin film with the distinct helical columns 70 terminating distally from the substrate 10 in a region of denser material forming a cap 74 for the helical columns. The cap 74 may be produced by changing the angle of incidence of the flux from θ near 90° to zero (as in Fig. 2) as described above (corresponding to rotation about an axis parallel to the substrate surface), or, it is believed on reasonable grounds that, the deposition of the helical columns may be ended under conditions giving rise to a higher diffusion length, as for example higher substrate temperature or changing to a lower melting point material. Increased substrate temperature may be created by exposing the substrate to light from quartz lamps. Temperatures of within about 100°C to 200°C of the melting point of the material being deposited may be required to create conditions of high diffusion length.

In these cases, the substrate 10 is planar. If the substrate 10 is not planar, a mask may be used to expose the substrate 10 to vapor only through slits in the mask and thus control the angle of incidence of the vapor. The mask may then be moved across the substrate to produce the desired thin film by sequential exposure of different portions of the substrate.

The desired pattern of film growth may also be tailored further. For example, a film may be started with a planar film of low porosity by rotating the substrate through exponentially increasing polar angles (zero to near 90°, as seen in Fig. 5C, area 48), with rapid azimuthal rotation (Fig. 5D), and then columns may be grown on the substrate 10, with or without rotation. In one embodiment of a tailored growth pattern, the substrate 10 is maintained at a constant polar angle (area 50 in Fig. 5C)

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while the substrate is repeatedly (a) rotated azimuthally a set number of degrees, for example 90°, and (b) held at a constant azimuthal position while the film grows obliquely, but linearly. The result is a helix with square sides in this instance. In general, the number of sides of the helix is $360/\gamma$, where γ is the number of degrees the substrate is rotated during periods of deposition.

In a further variation, the rotation of the motor 26 may be reversed during deposition to produce helices with sections of different handedness, one section having a right handed twist, and the other a left handed twist.

Since the deposition rate tends to vary considerably during deposition, to achieve helical growths with constant pitch, the rotation speed may need to be increased and/or decreased during deposition. In addition, by increasing/decreasing rotation relative to the deposition rate, helices with reduced/increased pitch, or helices with graded pitch may be obtained.

In general, the polar angle during an initial deposition period in which helical microstructures are to be produced should be greater than about 80°. The following table shows density of substances deposited as an obliquely incident vapor flux onto a substrate rotating about a normal to the surface of the substrate. The density given is the measured density of the helical film as a percent of the density of a planar film deposited at zero polar angle (normal incidence).

Table 1

Substance	Polar Angle in Degrees	% Density
Cu	85	46
Cu	88	37
MgF_2	85	32
CaF_2	75	19
CaF_2	85	9.3

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SiO	85	32
SiO	88	22
SiO	85	42
SiO	75	89
Al	85	32
Mn	85	52
Cr	85	27
Ag	85	52

While the porosity of CaF_2 at a polar angle of 75° is high, CaF_2 exhibits apparently poor structural features at 75°. The high porosity is believed to be due to the fact that CaF_2 molecules have extremely low surface mobility and thus, when molecules of CaF_2 collide with already deposited material, the molecules do not move far and they form very fine microstructures. By contrast, SiO at about 70° polar angle produces a layered structure without well defined helices.

Fig. 6 is a micrograph of helical growths of MgF_2 on a glass substrate. Source material was evaporated by resistively heating a filled tantalum foil boat in a vacuum chamber with pressure 1×10^{-6} torr. The polar angle was 85°. The growth shown here used feedback from the deposition rate monitor to ensure a film growth with constant pitch (w). Helices of similar form have been grown with pitches ranging from 50 to 9,000 nm, and in films composed of MgF_2, SiO, CaF_2, Cr, Mn, Ag, Si, Co, ZrO_2, Ti, Permalloy™ (85% nickel, 15% iron alloy) and Cu. It is believed on reasonable grounds that the process will work with any column forming depositable material. Depositable material is column forming when it exhibits limited adatom diffusion and a sufficiently high sticking factor that structures are formed, rather than unformed masses. Tests show that the MgF_2 helical film growths thus produced exhibit optical rotatory dispersion when $\lambda_{vac} > n_{avg}w$, where λ_{vac} is the wavelength of light in a vacuum and n_{avg} is the index of refraction of the MgF_2 film. The MgF_2 film has been found

to exhibit optical rotation approximating 340 degrees/mm in a film with 17.3 turns and w = 360 nm. Optical rotation for MgF_2 is counterclockwise for a right-handed helix, and clockwise for a left-handed helix.

As shown in Fig. 8, small mounds 80 may be micromachined or otherwise formed on the substrate 10 to form preferred locations for helical growths to initiate growth. The mounds 80 should be sufficiently close that shadowing effects prevent deposition of vapor between the mounds. In the case of mounds 80 having a height in the order of 1 micron, the mounds 80 should not be more than a few microns apart in case of the angle of incidence of the vapor being greater than 80°. The desired separation of the mounds 80 depends on the height of the mounds, the angle of incidence of the vapor, and the diffusion length of the vapor. An approximation of the separation L is given by L = $htan\theta$ where h is the height of the mounds. The mounds may have any shape, but the diameter is preferably selected so that only one column grows on each mound. The mounds 80 restrict growth of helixes to the mounds 80, and thus the growths can be forced to grow in specific locations. Various patterns of mounds for growing helical collumns can be made such as one shown in Fig. 9. The mounds can be used to grow slanted columns (no rotation of the substrate), and can be used to grow helices (with rotation of the sustrate. Control of the separation of the columnar growths is believed to be useful in applications such as operation of the thin film microstructure as a delay line, where the acoustic wave characteristics depend on the spacing of the helical columns, or use of the thin film microstructure as a biological filter.

Applications for the sculpted thin film helical growths described here include uses as helicoidal bianisotropic media, which are useful in a wide range of

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applications, as for example as isolators, circular polarizers, quarter-wave and half-wave plates, frequency converters and notch filters. When used as helicoidal bianositropic media, the vapor deposited material should be at least partially transparent at the wavelength of the electromagnetic radiation of interest. The helical growths 70, illustrated in Fig. 7A, deposited on a substrate 10, and grown with rotation of the substrate about a normal to the surface of the substrate, (with or without capping) may be sandwiched between two transparent charged electrodes 72 as shown in Fig. 7C. The electrodes 72 are shown schematically and in practice may be thicker. The electrodes 72 may be made from indium tin oxide or other transparent electrically conducting material and may take the form of plates, or may be patterned, particularly the top electrode. The cap 74 is preferably made from the same material as the helical growths, but need not be. When used with bounding electrodes such as those shown in Fig. 7C, the cap 74 and substrate 10 act as insulators. If insulators are not required in an application, then the substrate 10 may be conducting and the cap may form the upper electrode. As shown in Fig. 7D, plural top electrodes 77 may extend in parallel strips across the top of the cap layer 74. In this embodiment, the lower electrode 72 is formed on top of the substrate 10 and the columns have been grown directly from the electrode 72.

The structure shown in Fig. 7C may be used as an optical filter for circularly polarized light. By applying a charge to the electrodes 72, the electrodes 72 may be pulled together or pushed apart and thus change the pitch of the helices 70. This has the effect of tuning the filter created by the thin film.

In a further application, particularly of the helical growths 70 as illustrated in Fig. 7B with a cap 74,

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pairs of electrodes 76 and 78 may be placed at opposed ends
of the structure spaced from each other. A varying voltage
may be applied to one electrode 76 to sequentially compress
and expand the structure, with the helical columns thus
5   functioning as microscopic springs, in a direction parallel
to the helices 70 in accordance with the varying voltage.
The series of compressions and expansions will then
propagate along the structure as an acoustic wave to the
other end where the electrodes 78, acting as a capacitative
10   acoustic wave sensor, convert the acoustic wave to an
electrical signal. Such a device may act for example as an
electronic delay line, with a long delay in a very short
structure.

When the electrodes 72, 76, 77 and 78 are used as
15   sensing devices, which sense relative movement of the
electrodes bounding the thin film structure, the thin film
structure may be used for example as a microphone,
detecting acoustic waves, a pressure sensor or a force
sensor. Piezoelectric materials may be used as the material
20   from which the columns are made.

A capped structure such as the structure shown in
Fig. 7C or 7D may also be used as a pump or filter. When
the thin film structure is used as a filter, electrodes may
not be required. When used as a pump, the embodiment of
25   Fig. 7D may have the electrodes 77 charged sequentially to
squeeze the columns 70 and create a pressure wave in fluid
in the thin film structure that urges the fluid along the
structure.

A capped structure such as the structure shown in
30   Figs. 7C or 7D, with or without electrodes, may be used
respectively as an active or passive aerodynamic coating.
The structures of Figs. 7B-7D may also be used as
mechanical actuators by applying a charge to the electrodes

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and moving the cap in relation to the substrate on a very fine scale.

The technique of changing the polar angle after columnar deposition may be used to cap films with slanted, curved, vertical or other variably shaped columns.

A cap for a porous microstructure may also be formed by exposing the porous microstructure to conditions in which the atoms in the vapor flux have a higher diffusion length than during formation of the porous microstructure, as by changing the substrate temperature or changing to a lower melting point material in the vapor flux. It will be understood that in performing the inventive steps described herein the film composition may be altered during deposition by changing the material in the vapour flux. This may occur during formation of a porous microstructure, immediately before capping, or even during capping to form a layered, composite structure.

Multiple layered shadow sculpted thin films may be made by growing further columns, including helical columns, on a cap such as cap 74 shown in Fig. 7B, capping the further columns, and growing still further columns. In this way, thin film may be grown with columnar layers interspersed with caps, or flat layers.

Other uses for capped thin films include applications in semiconductor integrated circuit fabrication such as very low dielectric insulators for high speed devices, electroluminescent devices, optical sensing systems, including sensing of adsorbed species, catalyst supports, micro-sieves, biocompatible substrates for tissue growth, thermal barrier coatings on high temperature cycling parts such as jet turbine blades, flat panel displays, thermoelectric cooling panels, solar absorbers, adhesive surfaces, electron emitters, tactile sensing for smart skins, magnetic devices, anti-reflection/low

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diel ctric   constant   coatings,   humidity   sensing   and
microfluid pumping systems.

Sputtering of a material is also believed to be useful as a source of vapor.

A person skilled in the art could make immaterial modifications to the invention described in this patent document without departing from the essence of the invention that is intended to be covered by the scope of the claims that follow.

Appendix A

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HELIX2.VI   Page
05/31/96 09:30 AM
Connector Pane

(HLIX2.V)

Front Panel

Initial Param		System Contr

Initial Param

5.00	Number of T		85.0	Angle of Inc:
500	Helical Pit		100.0	Tooling
1.00	Ratio of Vertical Growth Rate to Deposition Rat		1.0	Chopper Facto:
20.0	Initial Depositior			Wafer Chuck Motor Direction
400	Capping Layer Thickn			
10	Number of turns in ca			CCW CW

System Contr

Click below to

Step 1:   Step 2:   Step 3:   Step 4:
Position 1 Start Wafa Begin Depositiclose Shutter
Angle Moto Chuck Moto (Open Shutter Click here to

Test Mo   Chopper Motor   .eset   Turn Power OFF.
            OFF:

Deposition Rate Monit

OFF Acquire Deposition Rate From Crystal Monitor

Current Deposition

0.0
Manual Depositic
0.0
.0   0.0   00.0   0.0
20.00
0.0
Rate Toleran
.0
.0   0.0   0.0   0   0.00   50

System Stat

Current S

Chuck Motor Si   Step Ra
Stopped.   0.00
Position (de
0.00

Percent Comp:
.0   0.0   00.0

Flux Angle Motor   Step Ra
Stopped.   0.00
Position (de
90.00

Film Thicknes
0

0.00   0.00

HELIX2.VI
05/31/96 09:30 AM

Block Diagram
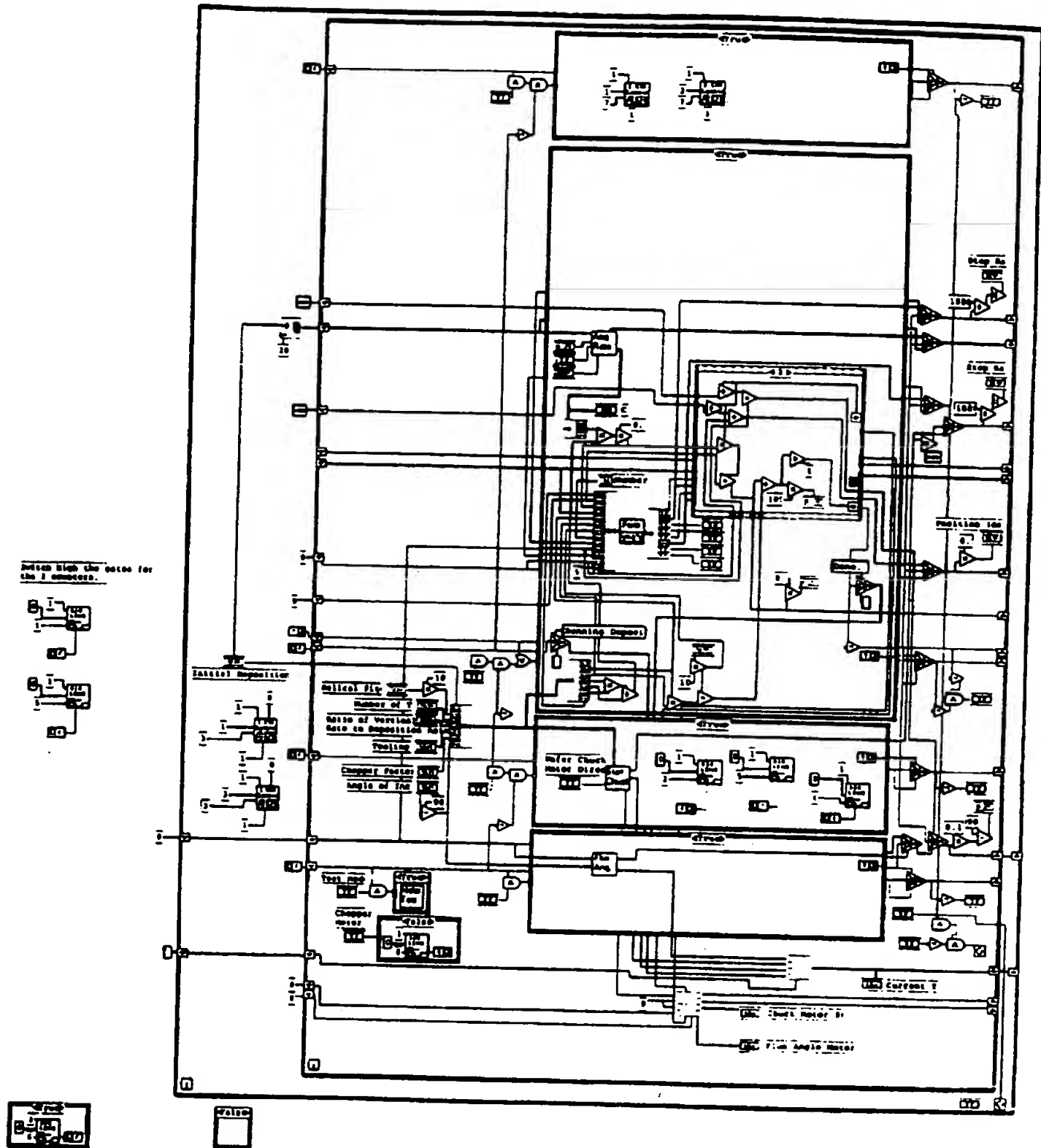
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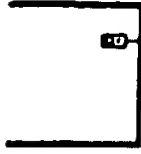
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05/31/96 09:30 AM
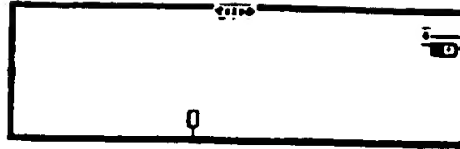
Appendix A

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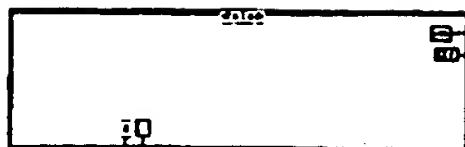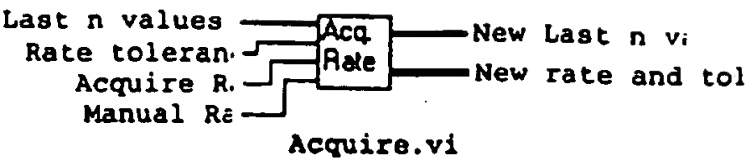
Page

Appendix A
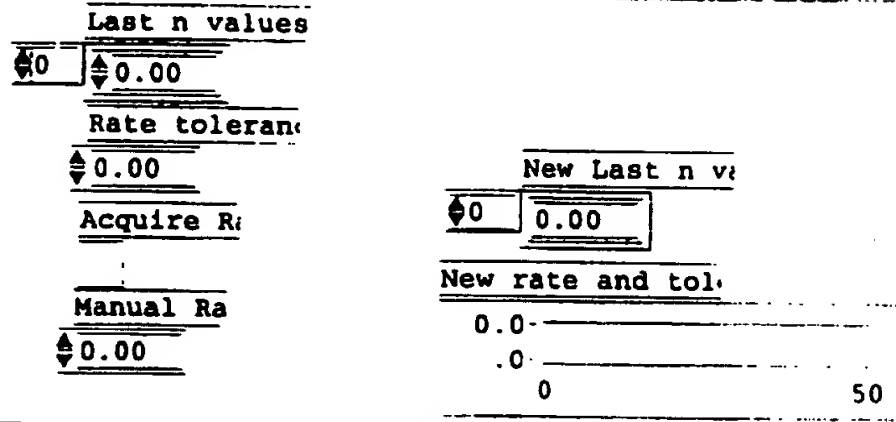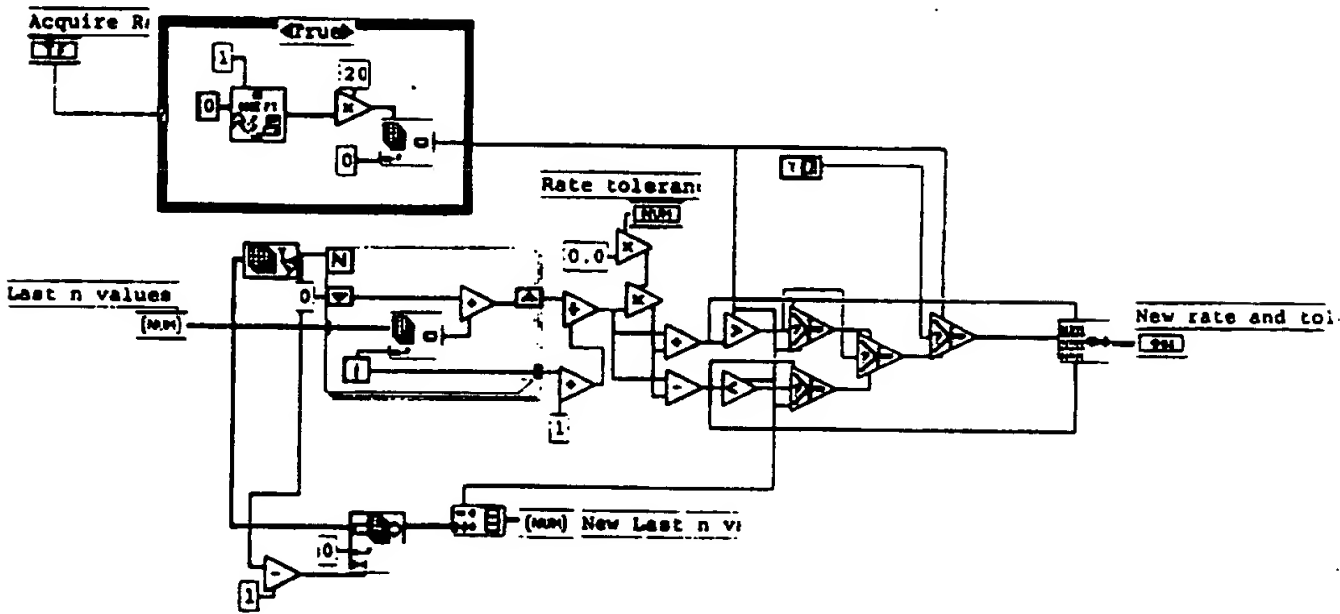
24

HELIX2.VI
05/31/96 09:30 AM

Page

Appendix A

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HELIX2.VI
05/31/96 09:30 AM

App ndix A

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HELIX2.VI
05/31/96 09:30 AM
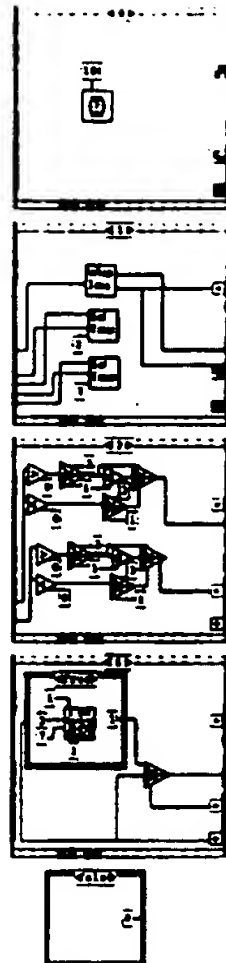
Page

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HELIX2.VI
05/31/96 09:30 AM

Page

Appendix A

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Acquire.vi   Page [Acq Rate]
05/31/96 09:34 AM

Connector Pane

```
Last n values ——┐ ┌Acq┐ ┌—— New Last n v
Rate toleran ——┘ │Rate│ └—— New rate and tol
Acquire R. ——┘ └———┘
Manual Ra ——
```
Acquire.vi

Front Panel

```
       Last n values
[0] [≑0.00]

       Rate toleran
[≑0.00]

       Acquire R

       Manual Ra
[≑0.00]
```

```
         New Last n v
[0] [0.00]

New rate and tol
0.0 ————————
 .0 ————————
  0              50
```

Block Diagram

Appendix A

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Acquire.vi
05/31/96   09:34 AM

Page

Acq.
Rate
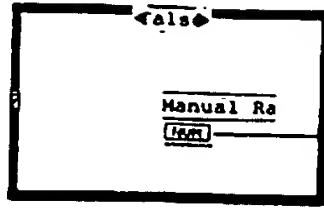
CHUCKMOT.VI
05/31/96   10:44 AM

Connector Pane

```
                              ┌─Start─┬───── Count for DAQ C.
Wafer Chuck Motor  [ ─────────│ Chuck │───── System St
                              └───────┘───── Motor S!
              CHUCKMOT.VI
```

Front Panel

Wafer Chuck Motor D

Count for DAQ C.
0.00

System St
|

Motor St
0.00

⬍ 0.00	Number of T	⬍ 0.0	Angle of Inc
⬍ 0	Helical Pit.		
⬍ 0.00	Ratio of Vertical Growth	⬍ 0.0	Tooling
	Rate to Depositi	⬍ 0.0	Chopper Facto)
⬍ 0.0	Initial Deposition		

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CHUCKMOT.VI
05/31/96 10:44 AM
Block Diagram

Appendix A

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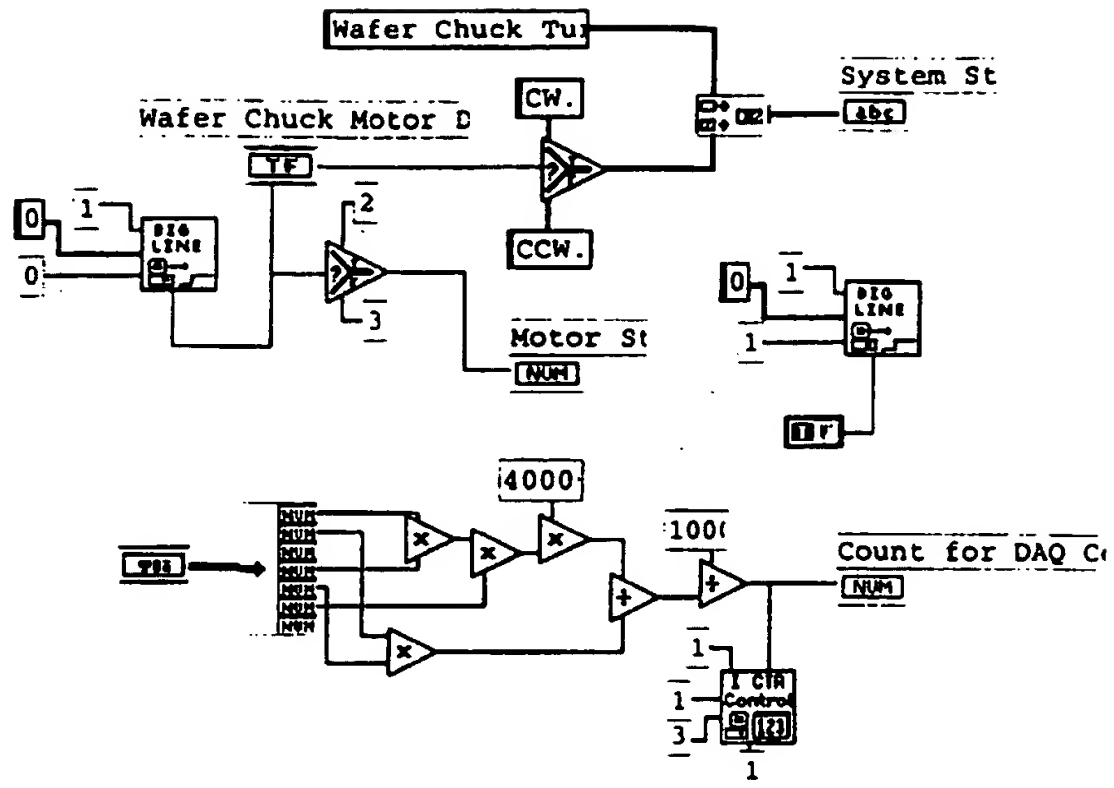
convtime.vi
05/31/96 10:47 AM

Connector Pane

Old Ti ── [Wrap Time] ── New Tin
                      ── Time Diffe
         convtime.vi
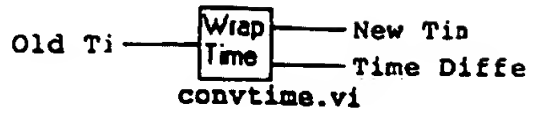
Front Panel

Old Ti	New Tin
0.00	0.00

Time Diffe:
0.00

Block Diagram

New Tin
[NUM]

True

Time Diffe:
[NUM]

Old Ti
[NUM]

0

Tnew=4294967295-
Told;
Told   Tnew

als
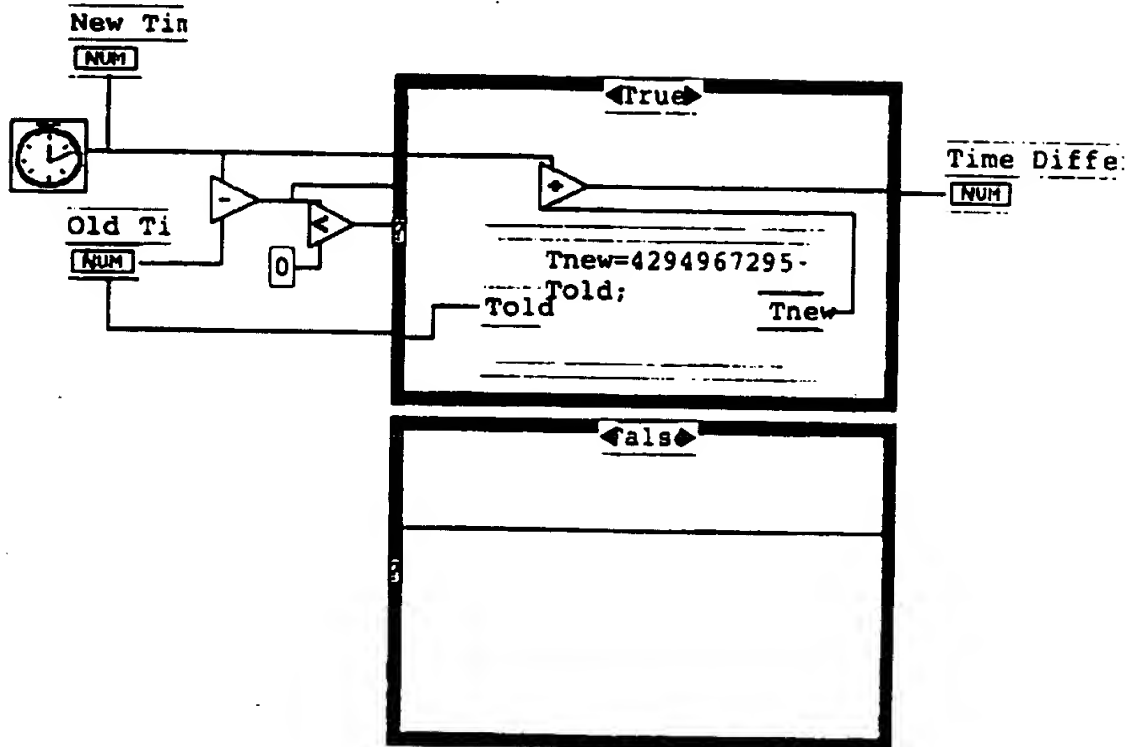
Appendix A

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Page [Flux Ang.]

fluxang.vi
05/31/96 10:48 AM
Connector Pane

Initial Positi ──── [Flux Ang.] ──── Final Position
Angle of Inc ────   ──── Output Mess
fluxang.vi

Front Panel

Initial Positi
⬍ 0.00

Angle of Inc
⬍ 0.00

Final Position
0.00

Output Mess
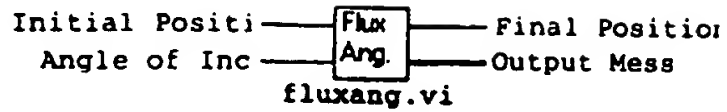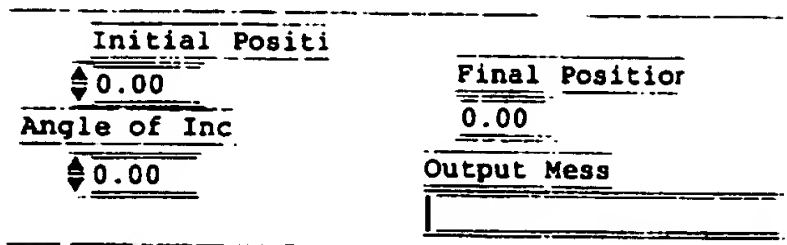
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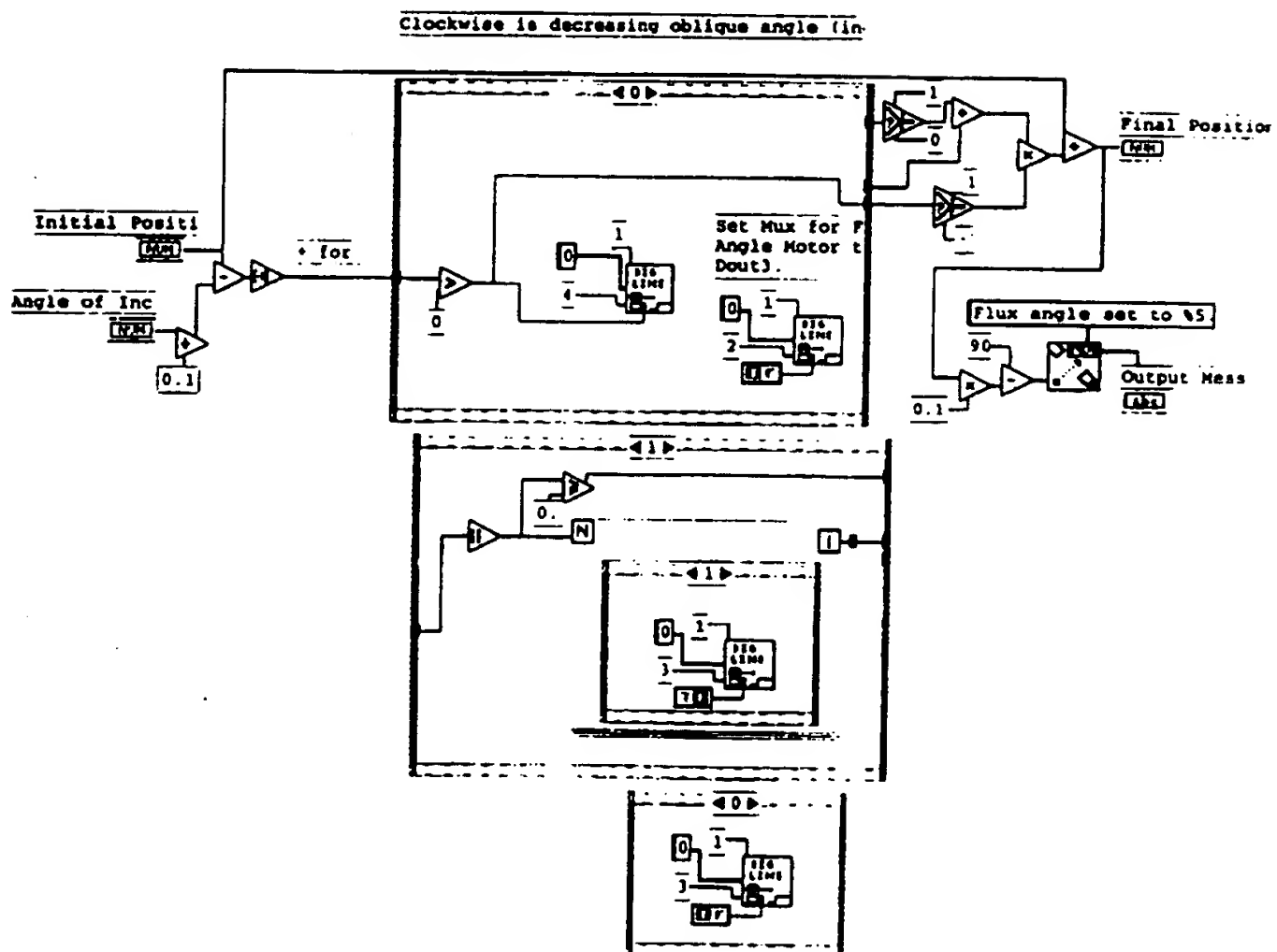
Appendix A

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FORMULA.VI
05/31/96 10:49 AM

Page [Form y=a'x]

Connector Pane

[Form y=a'x]
FORMULA.VI

Front Panel

Initial Flux Mot‹
0.00

Current Film Th
0.00

Film Growth
0.00

Time Differ
0.00

Film Pi
0.00

Film Tu
0.00

Capping Layer Thi
0.00

Capping Layer
0.00

Old Flux Motor Tim
0.00

Old Flux Motor
0.00

Old Chuck Motor Tim‹
0.00

Old Chuck Motor F
0.00

Rate Toler‹
0.00

Change Flux ‹

New Flux Timer
0.00

Flux Rate ‹

Flux Rate U₁

Change Chuck R

New Chuck Timer ‹
0.00

Chuck Rate O

Chuck Rate Un

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FORMULA.VI
05/31/96   10:49 AM

Block Diagram

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motstat2.vi
05/31/96 10:50 AM

Page [Motor Stat]

Connector Pane

Old Flux Angle Mot.
Flux Angle Motor
Chuck Motor St.
Chuck Motor St.
Chuck Motor St.
Old Chuck Motor
Flux Angle Motor

[Motor Stat]

Chuck Motor S
Flux Angle Motor
Chuck Motor S
Flux Angle Motor

motstat2.vi

Front Panel

Chuck Motor St.
0.00

Chuck Motor St.
0.00

Chuck Motor St.
0.00

Old Chuck Motor
0.00

Flux Angle Motor
0.00

Flux Angle Motor
0.00

Old Flux Angle Mot.
0.00

Chuck Motor S

Chuck Motor S
0.00

Flux Angle Motor

Flux Angle Motor
0.00

Block Diagram

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motstat2.vi
05/31/96 10:50 AM

Page Motor Stat.

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MOTTEST3.VI
05/31/96 10:51 AM

Connector Pane

Page   Motor Test

Motor
Test
MOTTEST3.VI

Front Panel

Test Mode

Turn Flux Angl.

tart

Turn Wafer Chuck

tart

Flux Angle Motor S   5.00

CCW   < —————— >   CW

00.0   .0   00.0

Chuck Motor Ste   5.00

CCW   < —————— >   CW

00.0   .0   00.0

Flux Angle Motor

Stopped.

Chuck Motor S

Stopped.

)one.

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MOTTEST3.VI   Page Motor
05/31/96 10:51 AM   Test
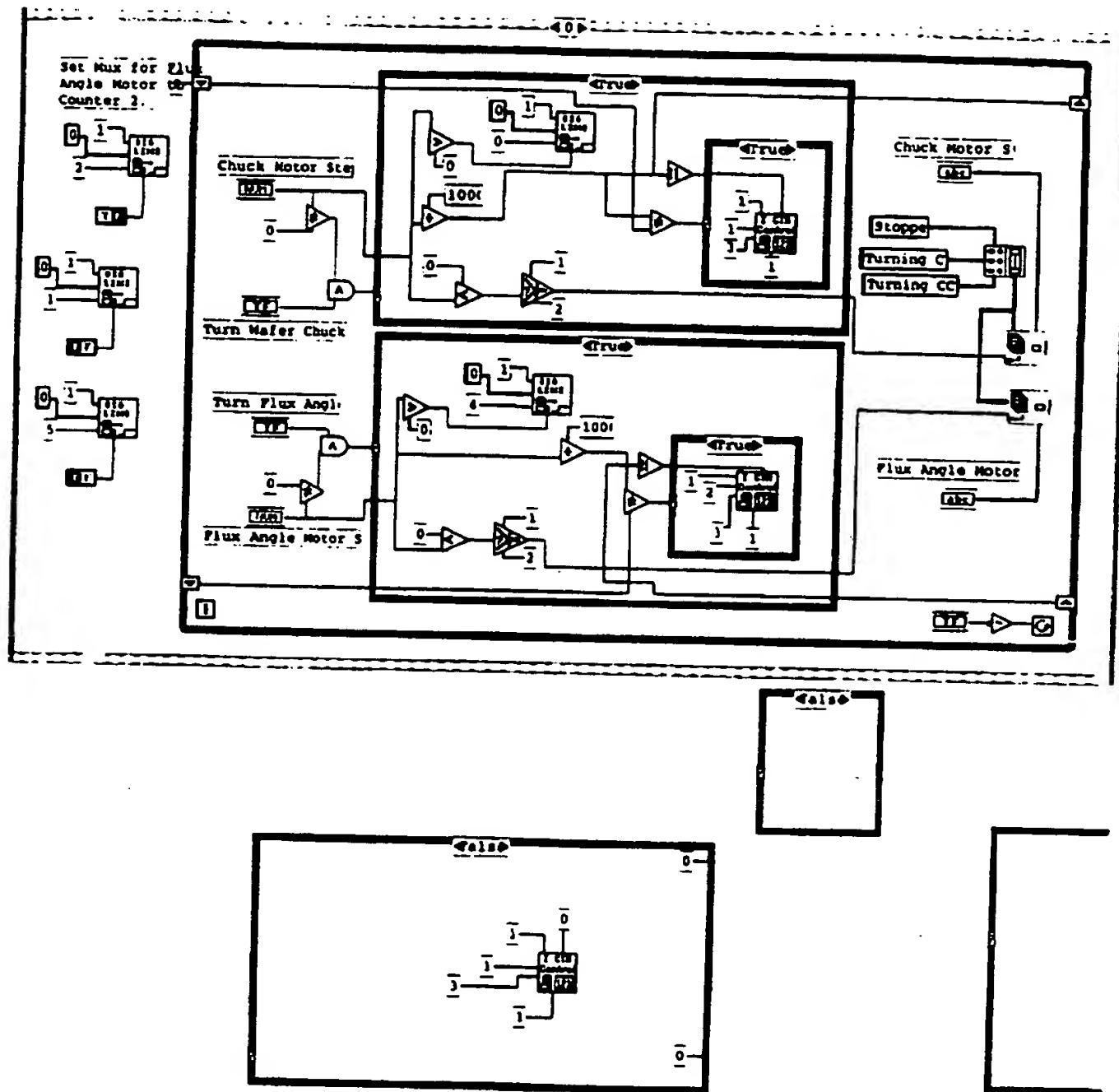
Block Diagram

Appendix A

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MOTTEST3.VI   Page Motor
05/31/96 10:51 AM   Test

Appendix A

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MOTTEST3.VI
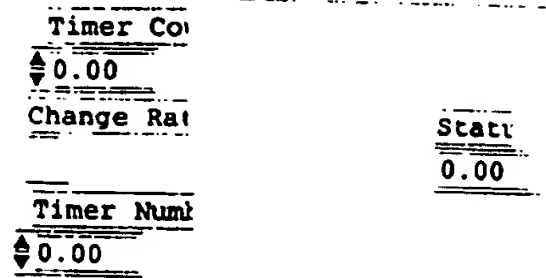05/31/96 10:51 AM

Page Motor
      Test

Appendix A

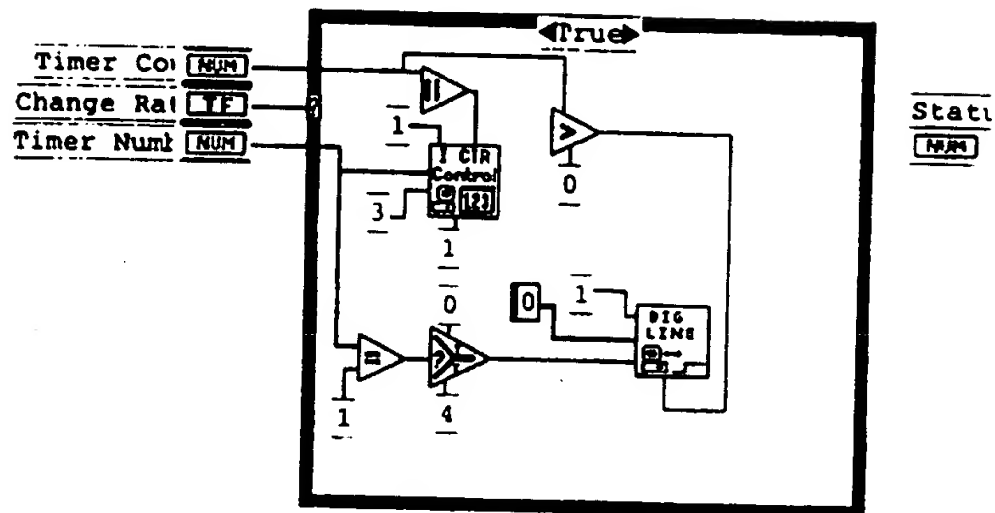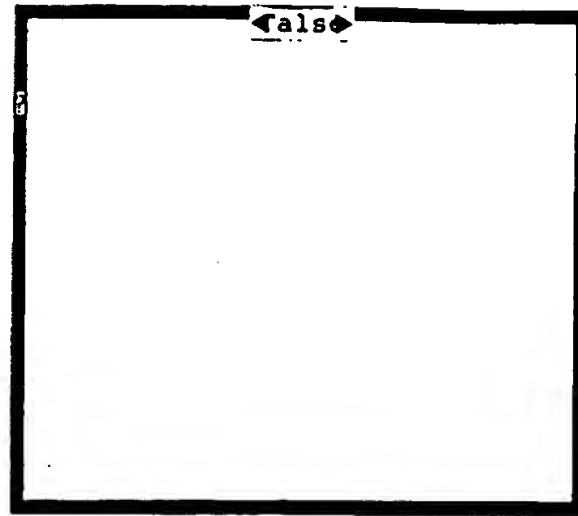settimer.vi   Page ┌─────┐
05/31/96   10:53 AM   │ Set │
                                                                                 │Timer│
Connector Pane   └─────┘

```
    Timer Co ────┌────┐
    Change Ra ───│Set │
                 │Timer├──── Stati
    Timer Num ───└────┘
              settimer.vi
```

Front Panel

```
   Timer Co
 ▲ 0.00
 ▼
   Change Ra                        Stati
                                    0.00
   Timer Num
 ▲ 0.00
 ▼
```

Block Diagram

Appendix A

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settimer.vi
05/31/96 10:53 AM

Page Set
      Timer

Appendix A

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Status.vi
05/31/96 10:55 AM

Page

Connector Pane

Last Va
Status
Status ──── Status Pick ──── Stat
Status
Status

Status.vi

Front Panel

Status :

Status :

Stat'

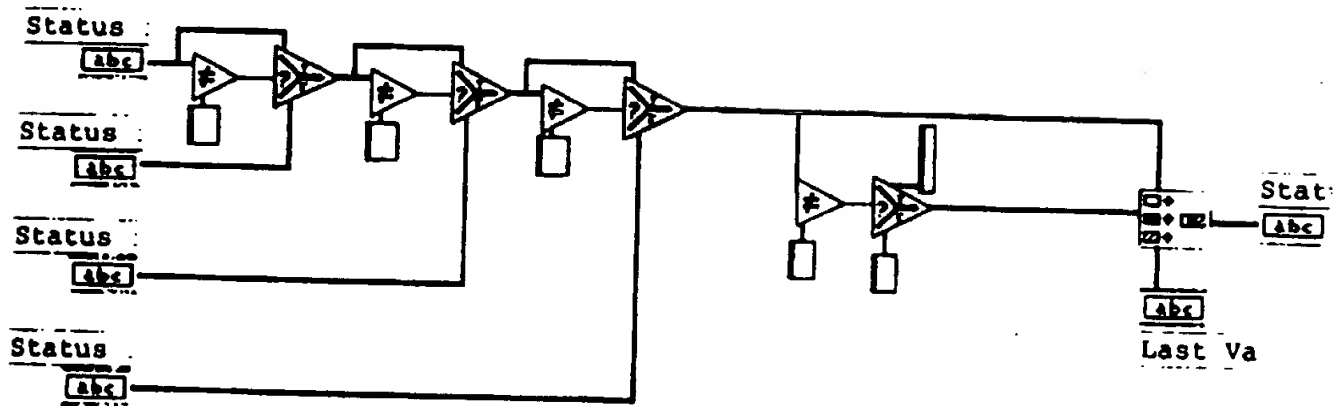Status :

Status :

Last Va

Block Diagram

Status :

Status :

Status :

Status

Stat'

Last Va

45
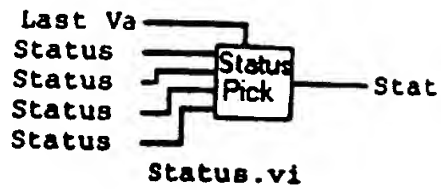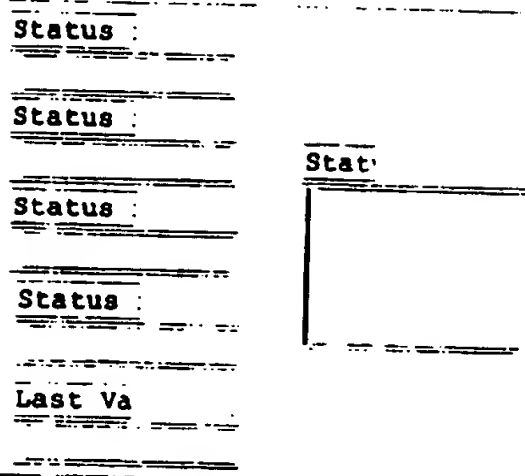
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1.   A method of sculpting vapor deposited thin films,
the method comprising the steps of:
            initially exposing a surface of a substrate to a
vapor flux at an oblique incident angle to grow a columnar
thin film; and
            forming a cap layer on the columnar thin film.

2.   The method of claim 1 in which forming a cap
layer on the columnar thin film comprises:
            while exposing the surface to vapor flux,
rotating the substrate about an axis parallel to the plane
of the substrate.

3.   The method of claim 2 further comprising, while
initially exposing the substrate to vapor flux, moving the
substrate to alter the direction of growth of the columns.

4.   The method of claim 3 in which moving the
substrate to alter the direction of growth includes
rotating the substrate about a normal to the surface of the
substrate to establish a helical thin film growth.

5.   The method of claim 4 in which the substrate is
rotated about the normal axis during the second
depositional period.

6.   The method of claim 1 further comprising forming
a cap on the columnar thin film by depositing material,
after formation of the columnar thin film, under conditions
of high diffusion length.

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7.   The method of claim 6in which conditions of high diffusion length are generated by heating the surface of the substrate.

8.   A thin film microstructure, comprising:
        a substrate;
        vapor deposited material extending in distinct columns from the substrate; and
        the distinct columns terminating distally from the substrate in a region of material forming a cap for the columns.

9.   The thin film microstructure of claim 8 in which the columns are made from material transparent to eletromagnetic radiation.

10.   The thin film microstructure of claim 8 in which the cap and substrate are each connected, respectively, to first and second electrodes.

11.   The thin film microstructure of claim 10 in which each electrode is a plate extending across the respective one of the cap and substrate.

12.   The thin film microstructure of claim 10 in which the first and second electrodes are connected at one portion of the thin film microstructure and an acoustic wave sensor is attached to the thin film microstructure spaced from the electrodes to permit propagation of acoustic waves through the thin film microstructure from the electrodes to the acoustic wave sensor.

13.   The thin film microstructure of claim 8 in which the columns are helical columns.

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14.   A method of growing thin film microstructures on a substrate exposed to a vapor flux at an oblique angle of incidence, the method comprising the steps of:

forming mounds on the substrate, the mounds being separated by sufficient distance that vapor is not deposited between the mounds; and

exposing the surface of the substrate to a vapor flux at an oblique incident angle to grow a columnar thin film on the mounds.

15.   The method of claim 14 further including:

rotating the substrate about a normal to the substrate during deposition to create helical growths.
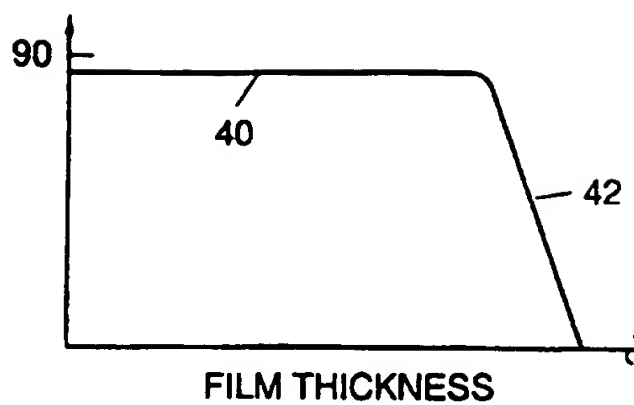
FIG. 1

FIG. 2

FIG. 3

FIG. 4

COMPUTER CONTROLLER

| AZIMUTHAL ANGLE CONTROL MOTOR | 26 |
| POLAR ANGLE CONTROL MOTOR | 24 |

STEPPER MOTOR DRIVE ELECTRONICS 28

LABVIEW INTERFACE 34

DATA ACQUISITION BOARD 32

30

DEPOSITION RATE MONITOR 36

FIG. 4A

MOTOR 24

MOTOR 26

29

27

10

11

25

FIG. 5A

POLAR ANGLE

FILM THICKNESS

FIG. 5B

POLAR ANGLE

FILM THICKNESS

FIG. 5C

POLAR ANGLE

FILM THICKNESS

FIG. 5D

1 REVOLUTION
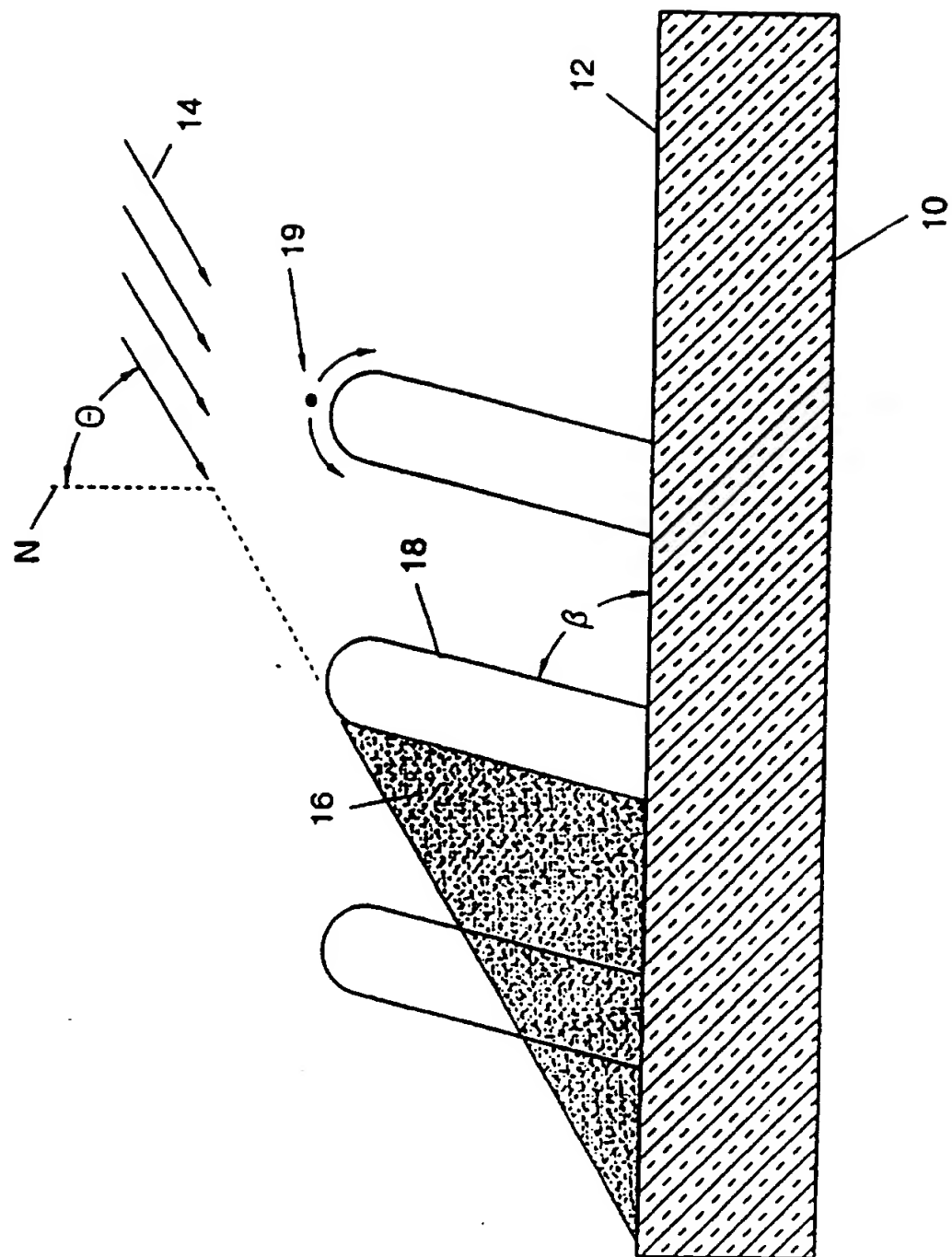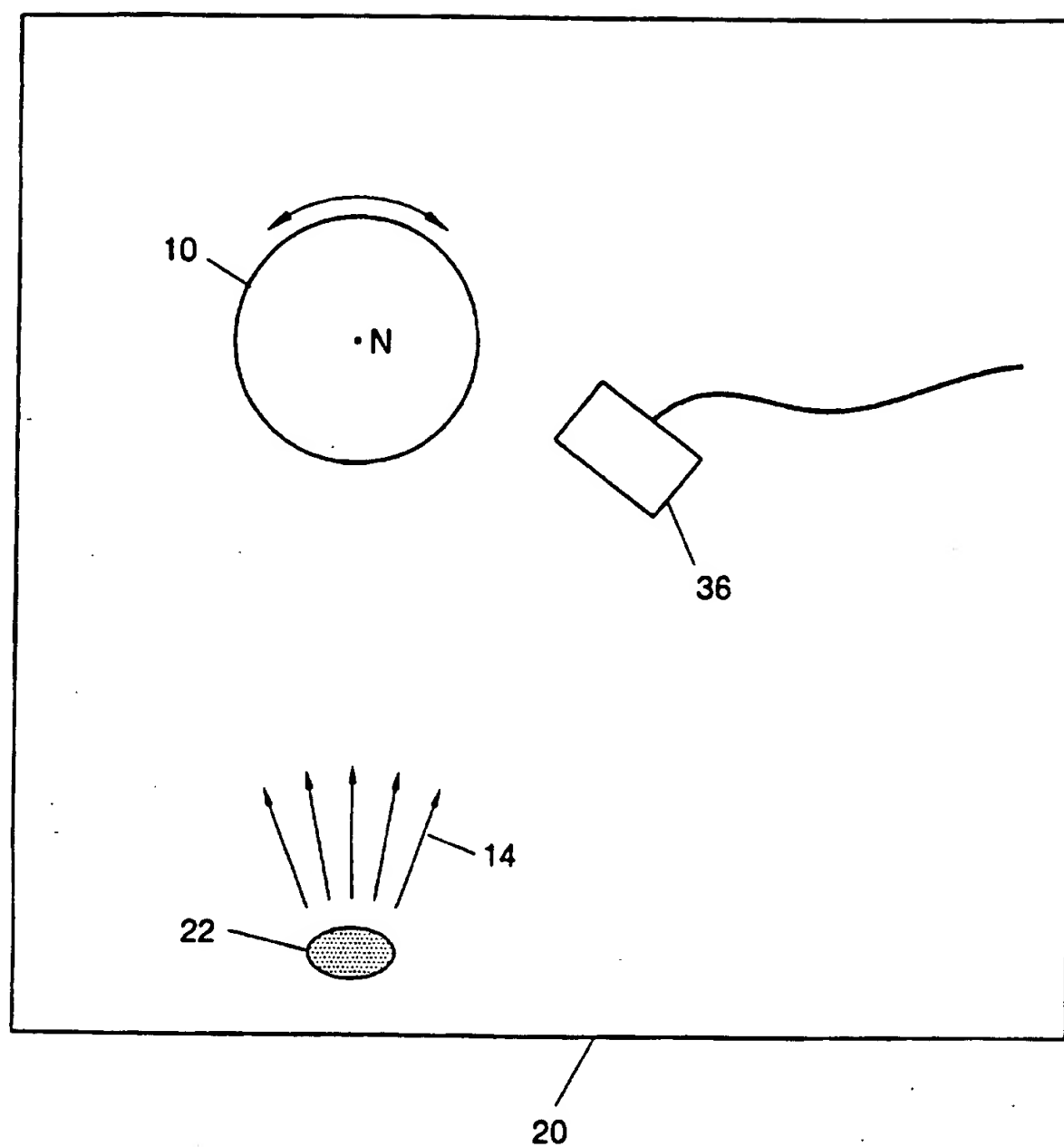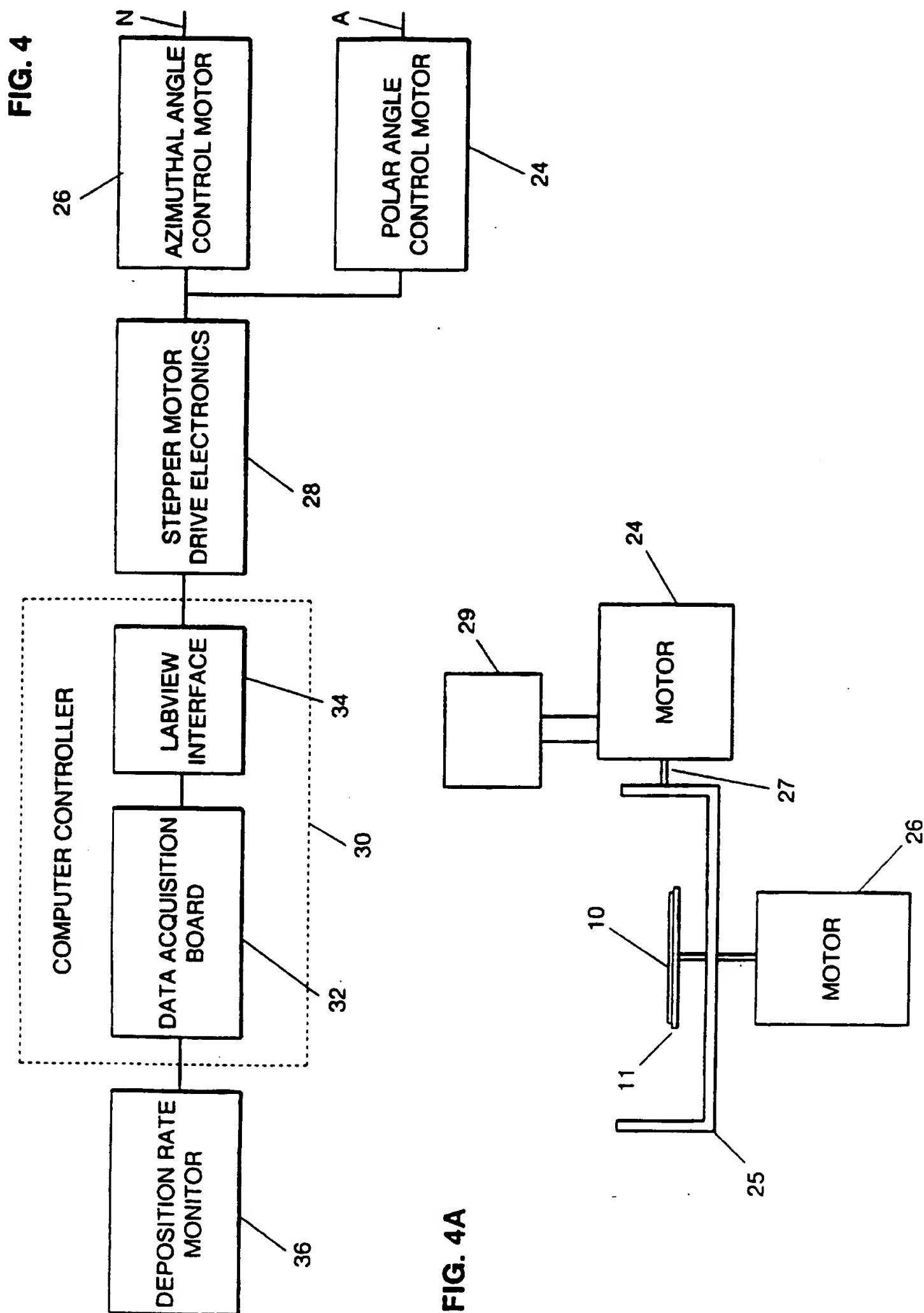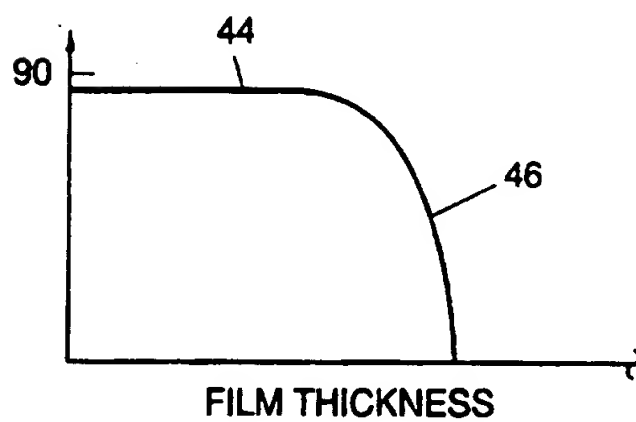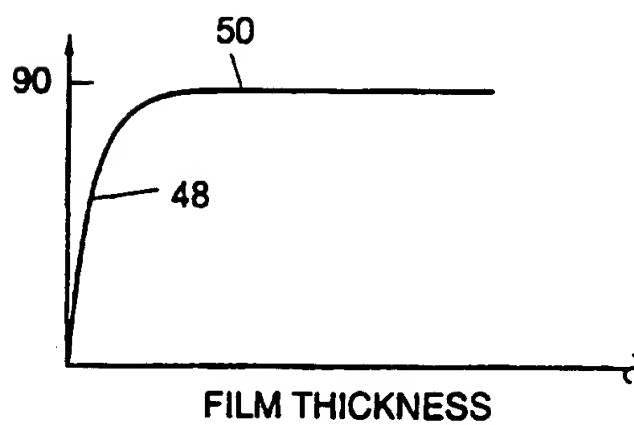
AZIMUTHAL ANGLE

FILM THICKNESS
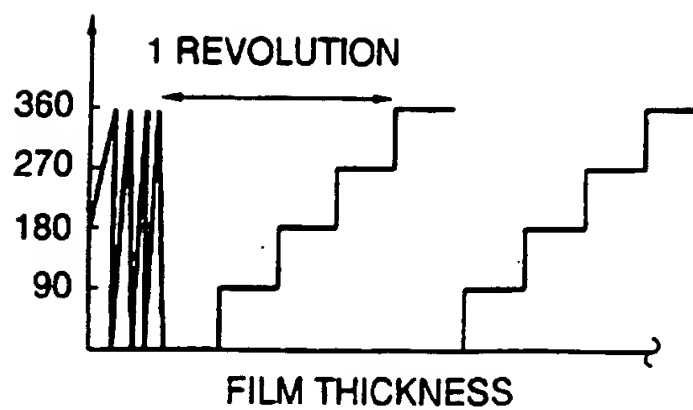
FIG. 6

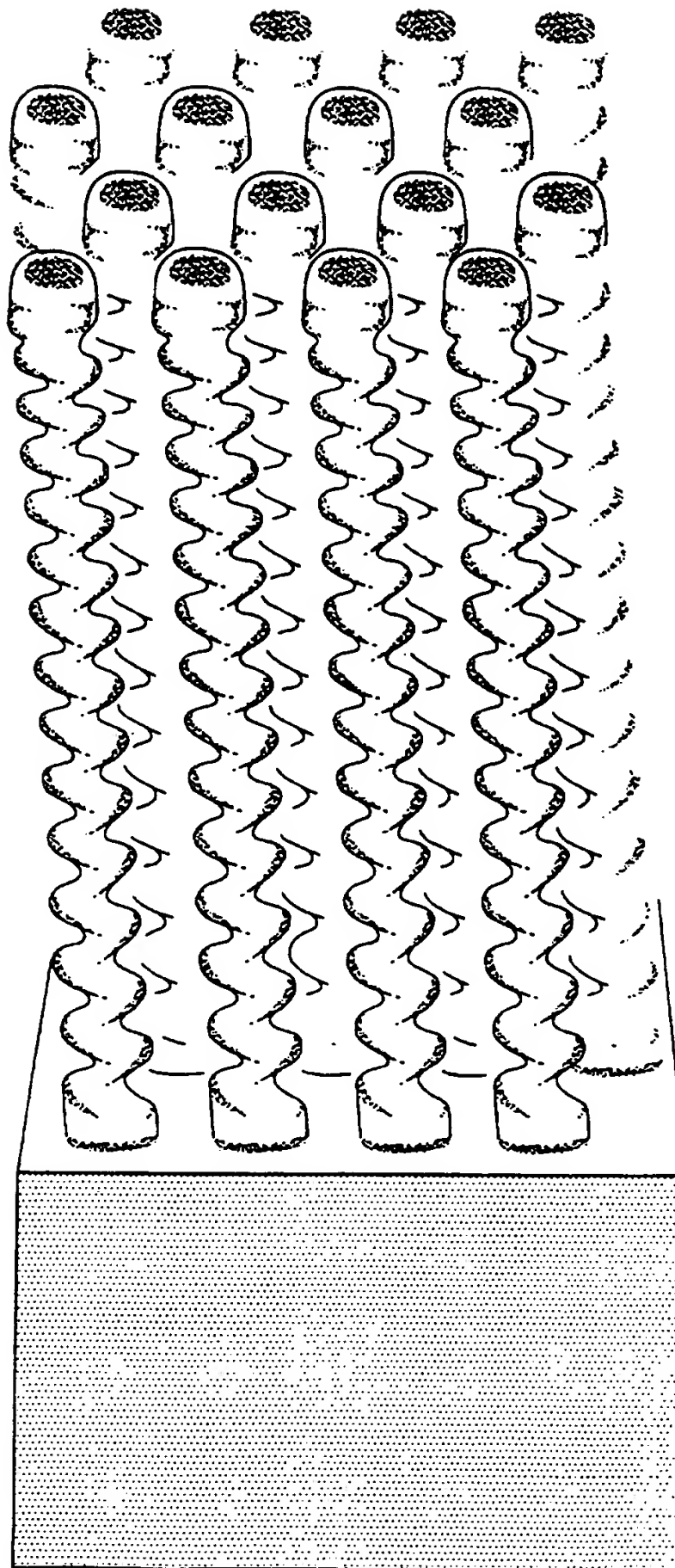5KV   1u
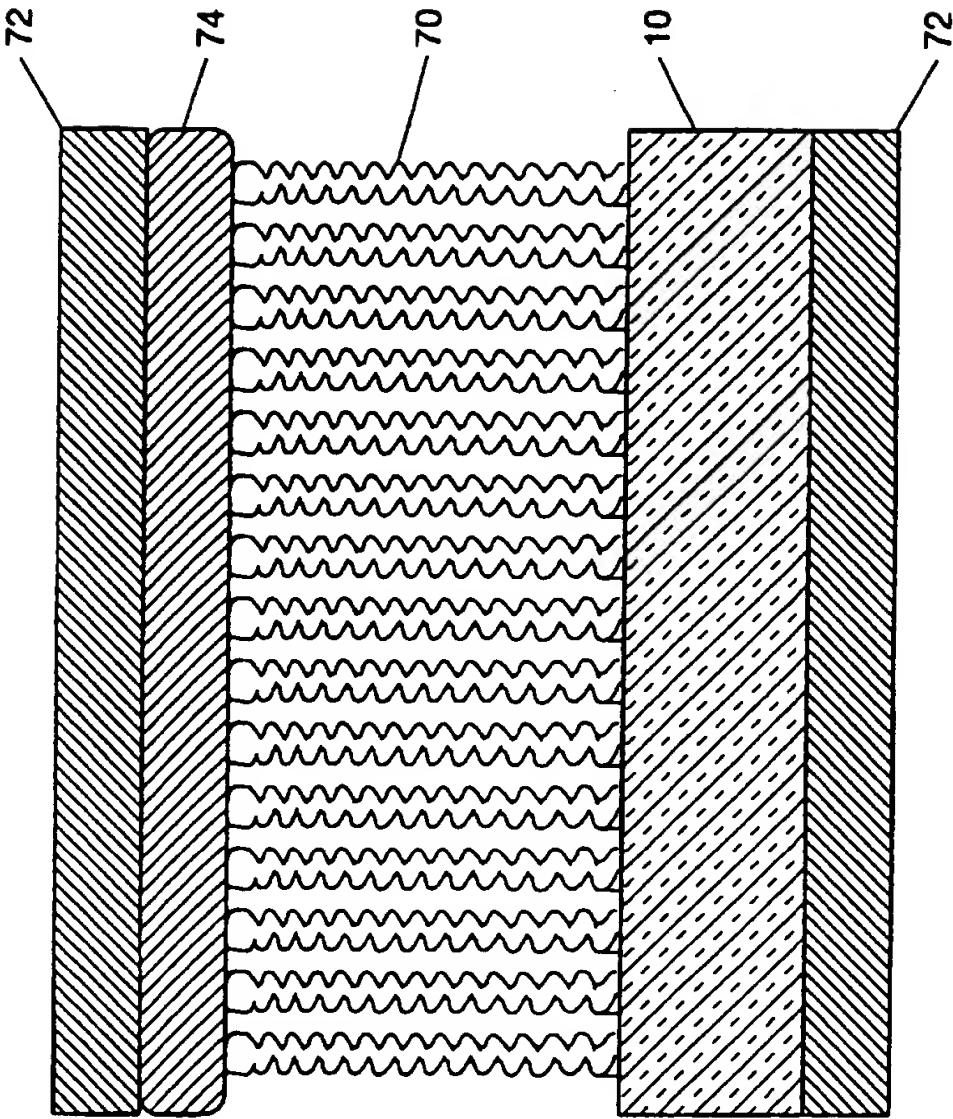   8 mm
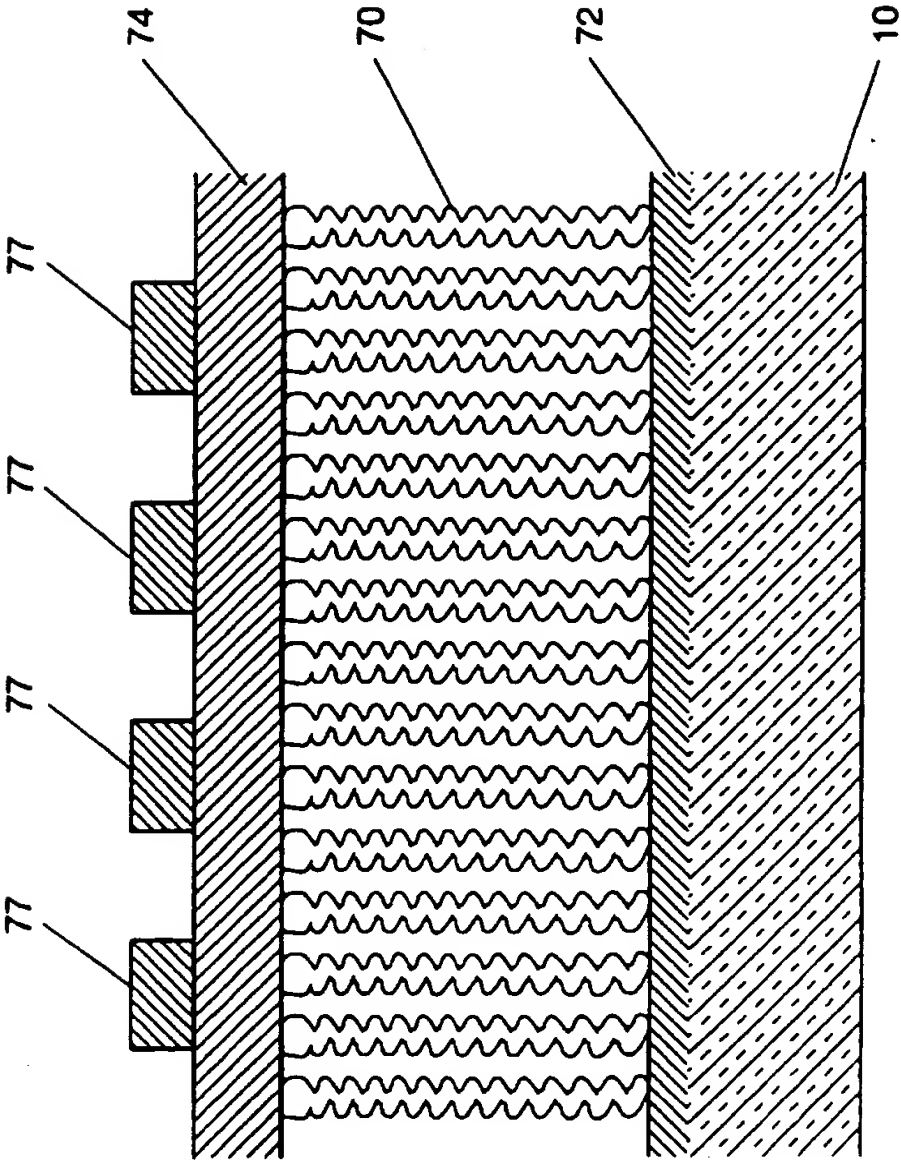
FIG. 7A
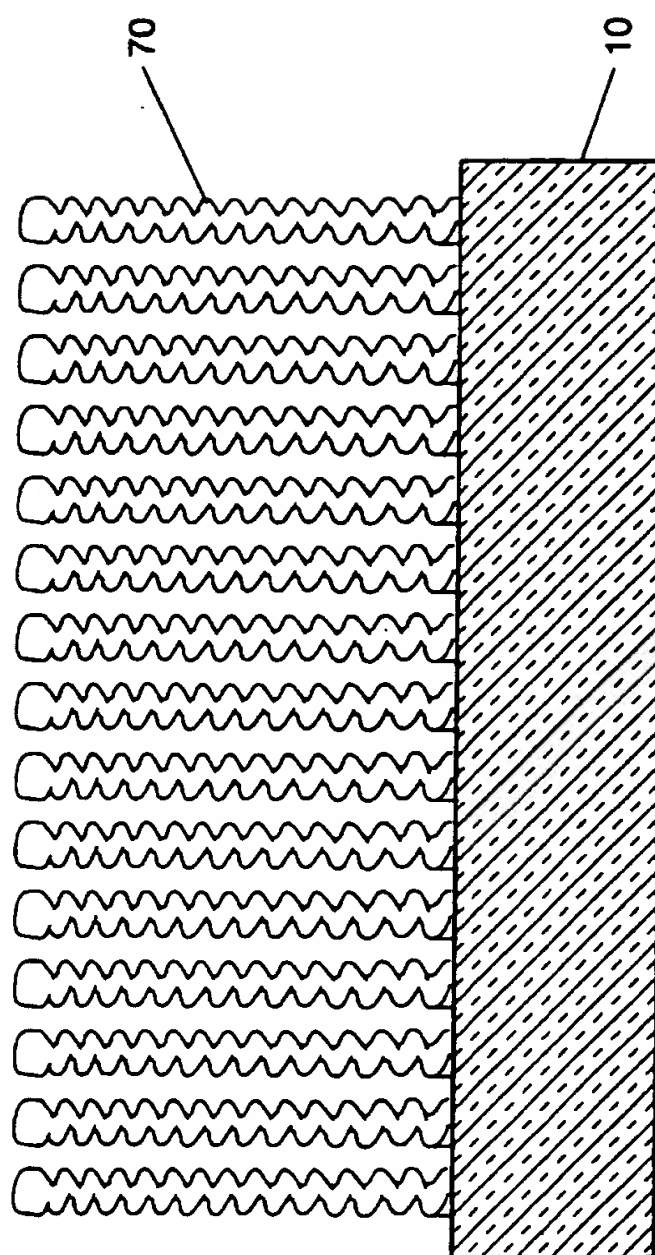
FIG. 7B
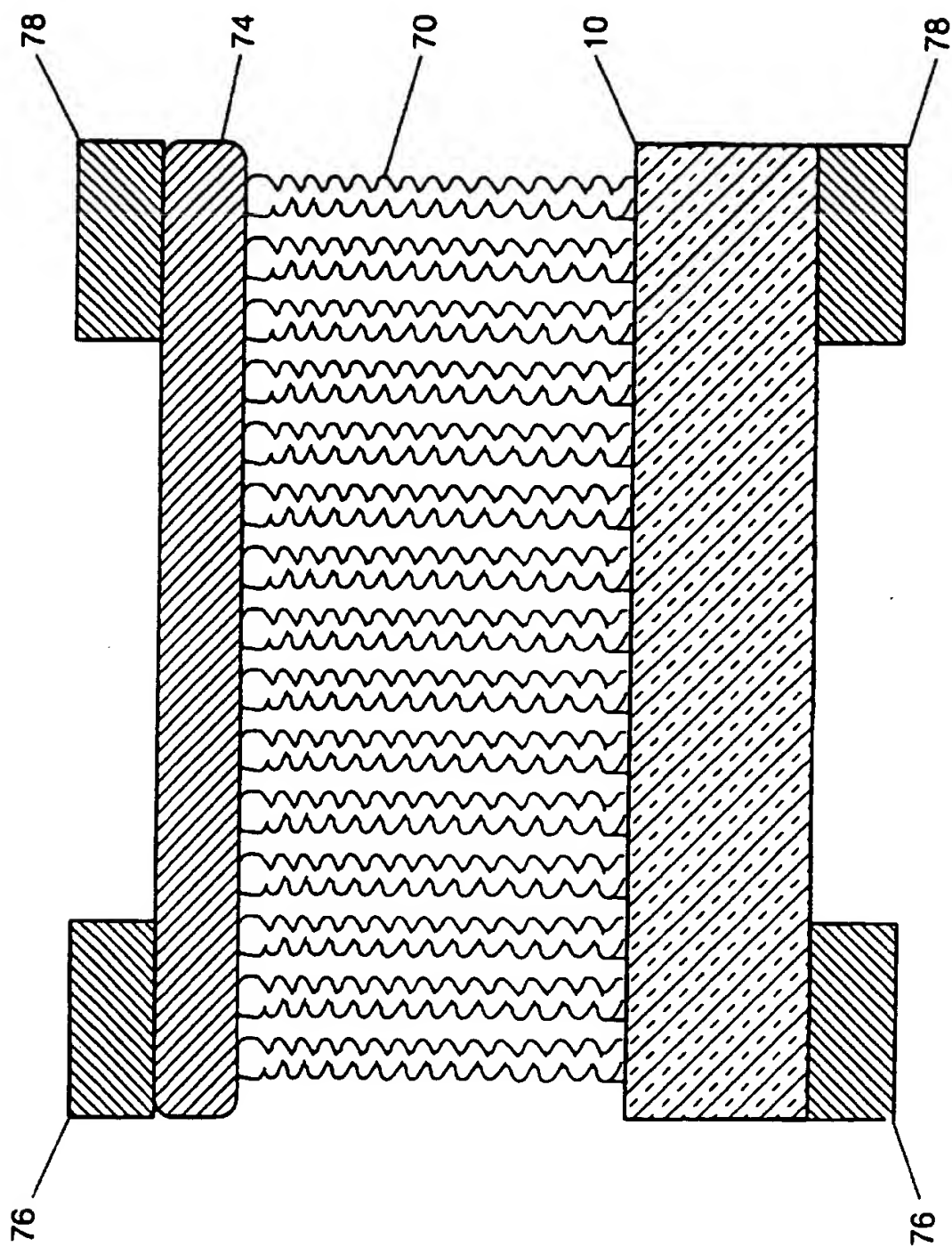
FIG. 7C

FIG. 7D

FIG. 8
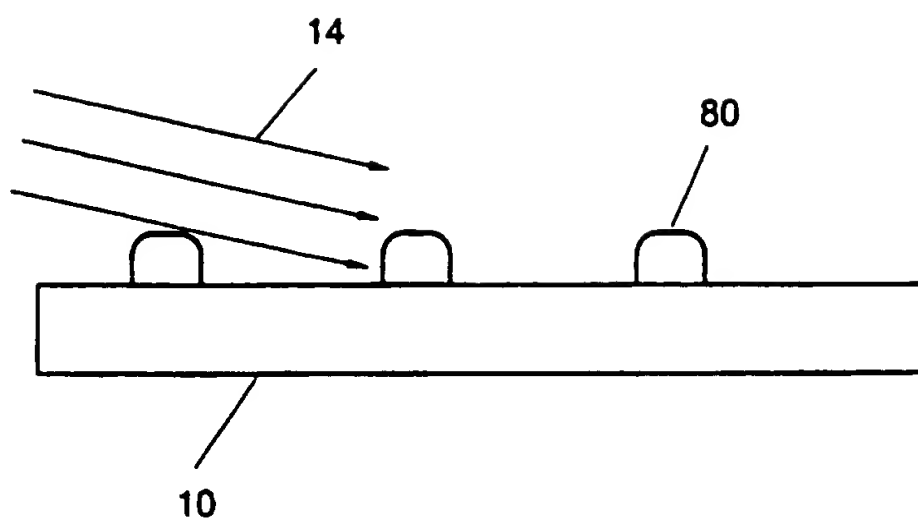
FIG. 9
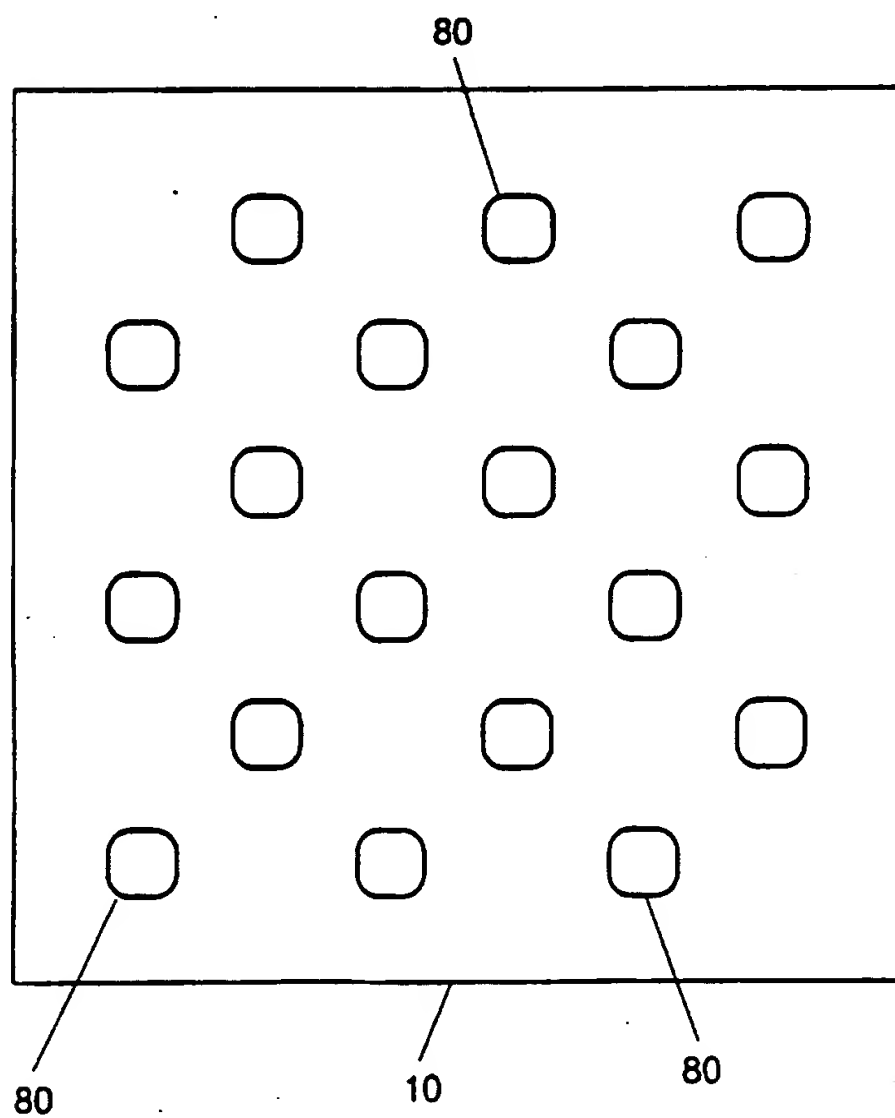
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C23C14/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 947 046 A (KAWABATA KATUICHI ET AL) 7 August 1990 see column 7, line 39 - column 8, line 5; figures 1-3 ---	1,8,14
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 352 (P-1248), 6 September 1991 & JP 03 134819 A (MATSUSHITA ELECTRIC IND CO LTD), 7 June 1991, see abstract ---	1,8,14
X	EP 0 517 411 A (HITACHI MAXELL) 9 December 1992 see the whole document ---	1,8
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 October 1997	1 4. 11. 97

Name and mailing address of the ISA	Authorized officer
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page 1 of 2

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 874 664 A (HAMAGUCHI SHIGEKI ET AL) 17 October 1989 cited in the application see abstract	1,8
A	ROBBIE K ET AL: "FIRST THIN FILM REALIZATION OF A HELICOIDAL BIANISOTROPIC MEDIUM" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 13, no. 6, 1 November 1995, pages 2991-2993, XP000555632 cited in the application see the whole document	1-15
X,P	ROBBIE K ET AL: "Sculptured thin films and glancing angle deposition: growth mechanics and applications" 43RD NATIONAL SYMPOSIUM OF THE AMERICAN VACUUM SOCIETY, PHILADELPHIA, PA, USA, 14-18 OCT. 1996, vol. 15, no. 3, pt.2, ISSN 0734-2101, JOURNAL OF VACUUM SCIENCE & TECHNOLOGY A (VACUUM, SURFACES, AND FILMS), MAY-JUNE 1997, AIP FOR AMERICAN VACUUM SOC, USA, pages 1460-1465, XP002044706 see the whole document	1-15

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 4874664 A	17-10-89	JP 63132201 A	04-06-88
		JP 1999331 C	08-12-95
		JP 7003486 B	18-01-95
		JP 63132203 A	04-06-88